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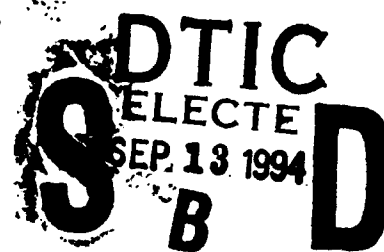
NMR RELAXATION STUDIES OF MICRODYNAMICS IN

CHLOROALUMINATE MELTS

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INTRODUCTION

Room temperature molten salts consisting of mixtures of $AlCl_3$ and 1-ethyl-3-methylimidazolium chloride (MEICl), are of interest as aprotic solvents for studying a wide range of both organic and inorganic compounds [1-7]. These chloroaluminate molten salts possess considerable potential as battery electrolytes and various types of electrochemical agents [8-10].

The composition of a chloroaluminate melt has a considerable effect on its physical properties. The variations in physical properties of the melt are due to a combination of factors including ion-ion interactions [4], and Lewis acid-base properties. Chloroaluminate melts with $AlCl_3$ present in excess (mole fraction, N, of $AlCl_3 > 0.5$) are termed acidic with $AlCl_4^-$ and $Al_2Cl_7^-$ the predominant anions.

The use of NMR relaxation methods provides useful information about the dynamics and structure of various chemical systems and chloroaluminate systems in particular. In a previous work[11], ^{13}C NMR relaxation measurements were used to investigate the motion and interactions of the MEI cation. The results indicate that $AlCl_4^-$ in a $Na^+_{0.22}MEI^+_{0.78}AlCl_4^-$ melt forms a complex by interacting with the C-2, C-4 and C-5 hydrogens on the MEI^+ ring. This investigation was followed by studies [12,13] in which the Dual Spin Probe method [14] supported the existence of $MEI(AlCl_4)_n^{(n-1)-}$ complexes in neutral ($AlCl_3 = MEICl$) and NaCl-buffered melts. ^{27}Al, ^{23}Na and ^{13}C NMR relaxation results confirmed the presence of the chloroaluminate-MEI^+ complexes and yielded ^{27}Al and ^{23}Na liquid state quadrupole coupling constants[12,13].

Application of the Dual Spin Probe(DSP) relaxation method typically requires knowledge of ^{13}C dipolar relaxation rates which are defined by (1), the basic equation in which the ^{13}C nucleus is relaxed by ^1H[15]:

$$R_1^{dd} = N_H(\hbar\gamma_C\gamma_H)^2 r_{CH}^{-6}\tau_{eff} \qquad (1)$$

where R_1^{dd} ($= 1/T_1^{dd}$) is the dipolar relaxation rate, N_H is the number of hydrogens attached directly to the carbon atom, γ_C and γ_H are gyromagnetic ratios and $r_{CH} = 1.09$ Å. τ_{eff} is the effective correlation time and varies *exponentially with temperature*. Equation (1) is operative while under the "extreme narrowing condition" ($\omega\tau_{eff} << 1$) which is usually applicable for small molecules including the chloroaluminate melts[11].

R_1^{dd} is obtained by measuring T_1, the Nuclear Overhauser Enhancement factor, η ($\eta_{max} = \gamma_H/2\gamma_C$) and using eqn (2) [16]:

$$R_1^{dd} = \eta R_1/1.988 \qquad (2)$$

The other part of the DSP method requires knowledge of quadrupolar relaxation rates for nuclei such as ^{27}Al and ^{23}Na. If there is a distortion from tetrahedral or cubic symmetry, nuclei such as ^{27}Al and ^{23}Na will be under the influence of an electric field gradient which produces the quadrupole interaction. The quadrupolar relaxation rate in the "extreme narrowing region" is given by(3) [15,17]:

$$R_1 = [3\pi^2(2I+3)/10I^2(2I-1)][1+(z^2/3)][e^2Qq/h]^2\tau_c \qquad (3)$$

where $I = 3/2$ for ^{23}Na and $5/2$ for ^{27}Al, eQ is the nuclear quadrupole moment, eq is the maximum component of the electric field gradient tensor, and z is the asymmetry parameter of the electric field gradient tensor($z = 0$ for $AlCl_3$).

The quadrupole coupling constant, QCC, is given by:

$$QCC = [e^2Qq/h] \qquad (4)$$

The DSP method has been applied to chloroaluminate melts[12,13] and has provided evidence that the ring hydrogens of MEI^+ interact with the tetrachloroaluminate anion. The existence of these complexes has been supported by linear plots of ^{13}C dipolar relaxation rates(R_1^{dd}) vs. quadrupolar ^{27}Al relaxation rates(R_1) that pass through the origin as predicted by equation (5):

$$R_1^{dd}(^{13}C)/N_H(\hbar\gamma_C\gamma_H)^2 r_{CH}^{-6} = R_1(^{27}Al)/\alpha\chi^2 \qquad (5)$$

where $\alpha = [3\pi^2/10][(2I + 3)/I^2(2I - 1)][1 + (z^2/3)]$, and $QCC = \chi$.

In this study, the DSP method is applied to melts containing MEICl, $AlCl_3$ and $EtAlCl_2$. The inclusion of $EtAlCl_2$ provides a "baseline" as there is a covalent bond between the ethyl group and aluminum in $EtAlCl_2$. The existence of covalent bonding(or complexation) between quadrupolar and dipolar nuclei in a molecule results in a linear plot of eqn. (5) that passes through the origin. In the MEICl-$EtAlCl_2$ melts reported herein, we observe a linear plot of eqn (5) that passes through the origin when applied to the terminal CH_3 carbon in $EtAlCl_2$ and one of the peaks in the ^{27}Al NMR of the melts.

EXPERIMENTAL

Materials

The 1-ethyl-3-methylimidazolium chloride (MEICl) and chloroaluminate molten salts were prepared as described previously [1]. Ethylaluminum dichloride (EtAlCl₂) was obtained from Aldrich. All materials were stored under anhydrous helium gas atmosphere in a dry box. All molten salt preparations and manipulations were performed in the dry box. Samples were loaded into 5 mm sample tubes, capped in the dry box, removed, and sealed immediately with a torch.

NMR Measurements

^{13}C and ^{27}Al NMR spectra were recorded on a Varian XL-300 spectrometer at 75.43 or 78.15 MHz. Temperature measurements were calibrated against methanol or ethylene glycol and are accurate to within 0.5°C. Pulse widths(90°) were typically 8.6 (75.43 MHz) and 7.6(78.15 MHz) μs. Longitudinal relaxation times were measured by the the inversion-recovery method

$(180°-\tau-90°-T)$ with $T > 10T_1$. At least 12 delay times(τ) were used and the results fitted to a three parameter exponential. NOE measurements were made using the gated decoupler method[18]. It is likely that the error in the NOE measurements is in the 5-10% range[18].

RESULTS AND DISCUSSION

The ability of both $AlCl_3$ and $EtAlCl_2$ to form C_{2H} dimers[19,20] led us to examine the ^{27}Al spectra of: (1) neat $EtAlCl_2$, (2) mixtures of MEICl-$EtAlCl_2$ and (3) ternary melts (N = $AlCl_3$/MEICl/$EtAlCl_2$)[21]. The neat $EtAlCl_2$ ^{27}Al NMR spectrum contains two peaks [21]. Peak 1 is a broad downfield peak that domi-nates the spectrum. The second peak (upfield) overlaps peak 1 and is only a fraction of peak 1 in total peak area. Peak 2 collapses into peak 1 as the temperature is lowered from 60 to 25°C. These two aluminum sites are consistent with the extent of monomer-dimer formation in liquid $EtAlCl_2$[21].

The MEICl-$EtAlCl_2$ (N = 0.5/0.5) melt ^{27}Al NMR spectrum also has two peaks. In this case, peak 1(downfield) is very broad while peak 2 is very sharp, and has a low peak area. Peak 2 increases slightly in area and peak 1 broadens as the temperature is lowered from 70 to 0°C. We have previously[21] made the tentative assignments of $EtAlCl_3^-$ for peak 1(downfield) and $Et_2Al_2Cl_3^-$ for peak 2.
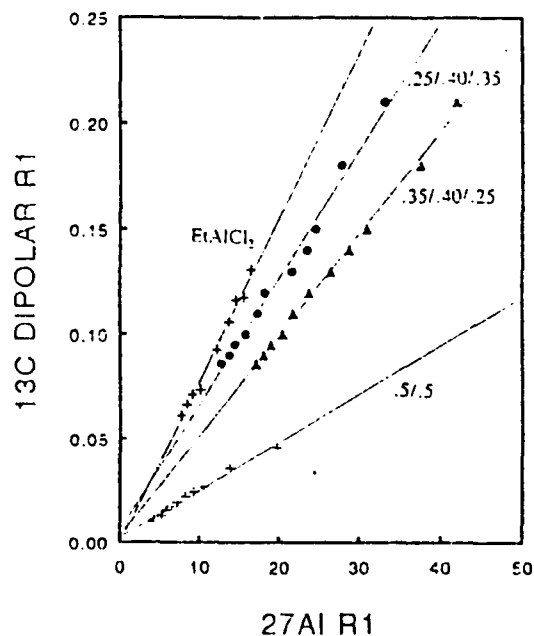

Fig. 1. ^{13}C Dipolar R1's vs ^{27}Al R1's(25 to 70°C) for Al peak 1 (127-131 ppm from $Al(H_2O)_6^{3+}$).

In this study, we first apply the DSP method to the CH_3 carbon in $EtAlCl_2$ and ^{27}Al NMR peaks 1 and 2 from several melt combinations and neat $EtAlCl_2$. Fig. 1 contains the results for ^{27}Al peak 1 (downfield) and Fig. 2 contains the results for ^{27}Al peak 2. The fact that both plots are linear and pass through the origin, indicate that: (1) the DSP method is appropriate for these systems and (2) the species associated with each peak contains $EtAlCl_2$. Furthermore, the slopes of these lines can be used to
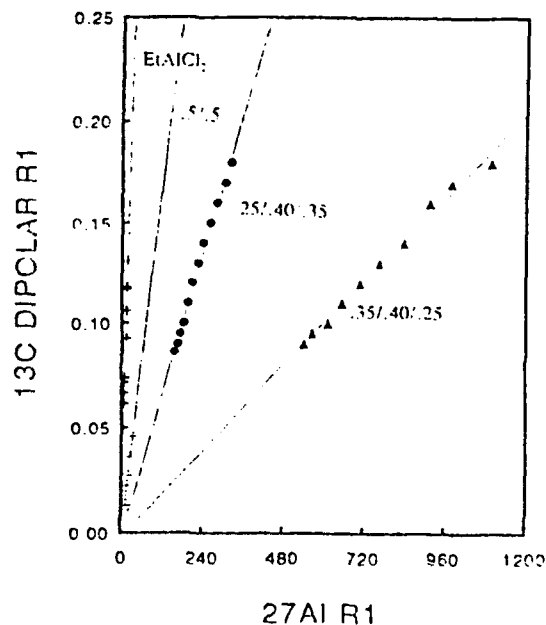

Fig. 2. ^{13}C Dipolar R1's vs ^{27}Al R1's(25 to 70°C) for Al peak 2 (102.5-103.0 ppm from $Al(H_2O)_6^{3+}$).

calculate the relative quadrupole coupling constants for the $EtAlCl_2$ -containing species in solution. The QCC values obtained from Fig. 1(Al peak 1) are 171, 119, 106 and 93 MHz for the (.5/.5), (.35/.40/.25), (.25/.40/.35) melts and neat $EtAlCl_2$, respectively. The QCC values obtained from Fig. 2(Al peak 2) are 6.9, 20, 11 and 93 MHz for the (.5/.5), (.35/.40/.25), (.25/.40/.35) melts and neat $EtAlCl_2$(repeated).

Results of the Dual Spin Probe method (eqn. [5]) applied to the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts indicate interactions between the Al-containing species in peak 2(102.5-103.0 ppm relative to $Al(H_2O)_6^{3+}$) and both the NCH_3 and ethyl terminal CH_3 groups of MEI'. Fig. 3 contains the plots for the NCH_3 group in each melt and Fig. 4 contains data for the terminal CH_3 on the MEI ethyl group.

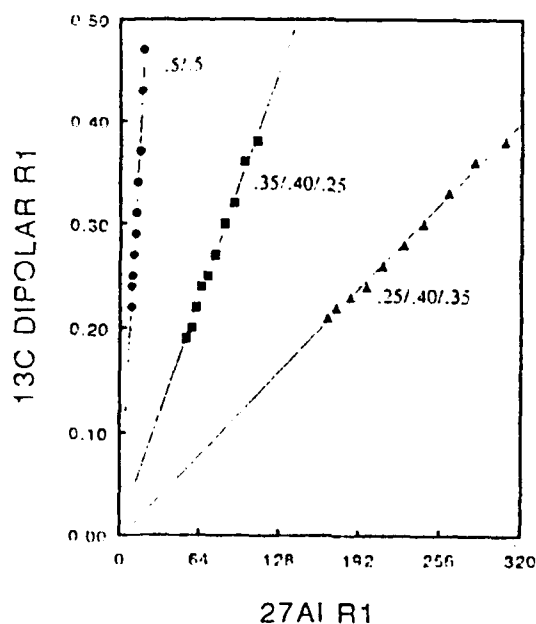Fig. 3. ^{13}C Dipolar R1's vs. ^{27}Al R1's(25 - 70 C) for NCH_3 carbon vs Al peak 2(25 - 70°C).
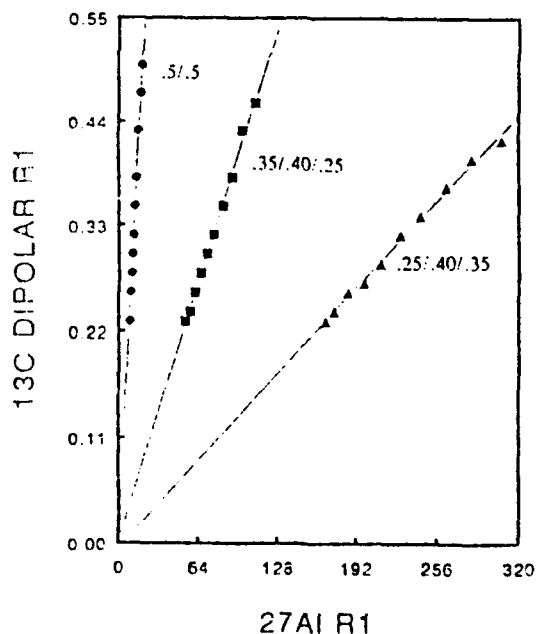
Fig. 4. ^{13}C Dipolar R1's for ethyl CH_3 carbon vs ^{27}Al R1's(25 - 70°C) for Al peak 2.

The QCC's obtained from the slopes in Fig. 3(MEI NCH_3) are 1.7, 2.3 and 4.4 MHz for the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts. The QCC's from

Fig. 4(terminal CH_3 on the MEI ethyl group) are 1.6, 6.9 and 1.3 MHz for the (.5/.5), (.35/.40/.25) and (.25/.40/.35) melts.

Finally, there is no correlation between the ring hydrogen dipolar R1's and any of the ^{27}Al peak R1's. This result is directly opposite to that found in MEICl-AlCl$_3$ systems [11,12].

CONCLUSIONS

Application of the DSP probe method to these mixed melt systems indicates a lack of complexation between the ring hydrogens of MEI^+ and any of these aluminum containing species. These and previous results[21] suggest that the formation of various charged dimers containing $EtAlCl_2$ takes precedence over the formation of complexes between $EtAlCl_3^-$ and the MEI^+ ring hydrogens. However, there is evidence of interaction between the various Al-containing species and the CH_3 groups(NCH_3 and terminal CH_3 in the ethyl group) of MEI^+ in these melts.

ACKNOWLEDGMENTS

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